

SYMPOSIUM ON FUEL CELLS
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RECENT DEVELOPMENTS IN HIGH-TEMPERATURE CELL RESEARCH
IN THE NETHERLANDS

By

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I. INTRODUCTION

Research on high-temperature fuel cells have been carried out in the Netherlands since 1950 by the Central Technical Institute of the Organization for Industrial Research T.N.O. Up till 1955, similar research has been done by Scholte and co-workers at the "Staatsmijnen" research laboratory at Geleen, partly in close cooperation with T.N.O. Results of the latter work have not been published, but they were fairly similar to those of T.N.O. An extensive survey, up till 1958, of the investigations by the Central Technical Institute has been given in a thesis (1) by one of the present authors. Some additional communications (2, 3, 4) on the same work were published in 1960.

During the period 1950-1958, laboratory cells were developed showing fairly good electric performances at 500°-750°C. on H_2 - H_2O , CO - CO_2 , CH_4 steam and similar gas mixtures, over quite long periods (viz. up to 6 months).

The small disk-shaped cells (about 5 cm dia.) had a sintered MgO -molten carbonate "semi-solid" electrolyte, sandwiched between two thin metal powder electrodes. The MgO ceramic carrier of 40-50% porosity provided the mechanical strength and simultaneously immobilized the liquid carbonate phase.

The major weakness of the cells was their insufficient electrolyte gas-tightness, caused by small cracks and gradually increasing numbers of open pores in the refractory MgO body. Although gas-tightness is an obvious and essential demand for any practical cell, it is very difficult to realize this completely with the mentioned electrolyte body. Nevertheless, it was felt that this problem must be solved before it will be possible to construct larger sized cells of real practical sense.

At our present state of knowledge, only molten carbonate electrolytes appear to be useful for high-temperature cells, this in connection with the necessary chemical stability against the cell reactants and their products, and the required low specific resistance. (The practical application of solid oxygen ion conductors in the range of 500°-800°C. seems very difficult.) (5) Therefore, our research with the electrolytes mentioned was continued from 1959 onwards. The use of refractory porous MgO electrolyte carriers involves a number of disadvantages:

1. MgO can be sintered only at fairly high temperatures (1300°C.) and sintering promoters may be applied only when they do not react with the carbonate melt to be impregnated afterwards.

2. Increasing, e.g., the diameter of ceramic disks, leads inevitably to increased fragility since their thickness must remain small (say less than 1 cm).

3. The rigid ceramic bodies, after impregnation with the melt, must pass twice the "dangerous" temperature region of the liquid-to-solid (and reverse) transition of the melt, namely upon cooling for assembling the cells and upon heating for operation. It was found that in the case of a ternary (Li-Na-K) carbonate mixture, the relative volume change at the melting point was more than 5%, so the formation of at least a few stress cracks in the MgO support seems very hard to avoid.

4. Although MgO is chemically inert against carbonate melts, it is slightly soluble in them. This was verified by qualitative tests. Recently, Janz and Lorenz (6) made similar observations. Owing to the dynamic character of the solid-solute equilibrium, it seems unlikely that the ceramic MgO structure will remain unaltered in the long run. Moreover, there might be a direct O^{2-} ion exchange between CO_3^{2-} and the MgO lattice ions. Some experiments with highly sintered porous MgO tubes*, exposed to

*Manufactured by "Degussa", Frankfurt a. m., Germany. ("Sintermagnesit Mg 24").

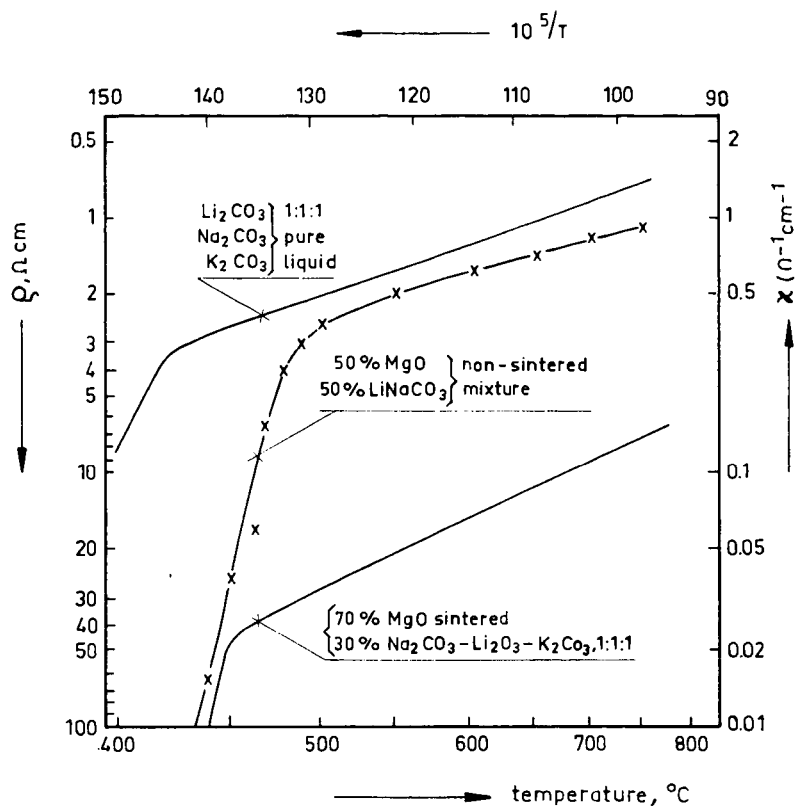


Fig. 1 Specific resistance (conductivity of liquid-paste-and sintered matrix electrolytes

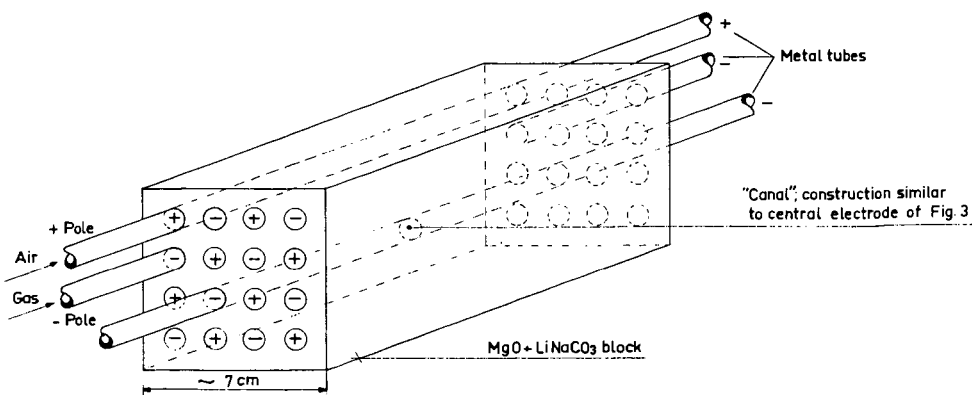


Fig. 2 Canal cell (schematically)

LiNaCO_3 melts at 700°C . for some weeks, indeed revealed a slow but steady disintegration of the ceramic structure. (Powdered MgO could be washed out of the pores.)

On the basis of these arguments, further experiments with refractory carriers were abandoned.

An obvious and technically sound approach towards complete gas-tightness is the direct use of liquid carbonates, e. g., as applied by Chambers and Tantram (7) and by Douglas, (8)

However, in that case the mechanical strength of the cell must be found completely in the electrode construction. A system of "double porosity electrodes", sintered onto backing plates, seems necessary to avoid pore flooding and gasbubble formation. Apart from the question whether or not these systems will withstand the prolonged exposure to the carbonate melt, the price of such highly refined units might be a serious drawback for electricity generation for non-specialized purposes on large scale.

II. PASTE ELECTROLYTES

In our opinion, it seems worthwhile to study a third alternative, i. e., the application of paste electrolytes which possibly combine the advantages of electrolyte immobilization and some mechanical strength with the avoidance of the ceramic body problems. The obvious method is to prepare pasty mixtures of an inert carrier powder (for which MgO serves well) and molten carbonates. (The approach is not a new one. Already Baur (9) applied similar mixtures as electrolytic bridges. Greger (10), too, mentioned their possible use. The idea, however, does not seem to have been worked out in detail.)

Preliminary experiments revealed that pellets (cold-pressed) from fine MgO powder and LiNaCO_3 (m. p. 510°C .) mixtures did not show any plastic deformation after 16 hours of heating at 700°C ., even when their carbonate content was as high as 50% by weight.

In a further test the relation was studied between the MgO particle size range and the "maximal" amount of LiNaCO_3 that could be mixed with the MgO powders, without the mentioned deformation under their own weight. Observations were made with pellets of 1.3 cm dia. and 1.5 cm thickness, cold-pressed from different relative amounts of MgO and carbonate. The pellets were first baked during 24 hours at 700°C ., whereafter their shape was observed. Then they were baked another 24 hours at 850°C .. It was found that all pellets that did not deform at 700°C ., neither did so at 850°C .. This means that the viscosity of LiNaCO_3 melt bears no detectable influence upon the consistency of the substance. The results of this test are given in Table I. Strong deformation (nearly liquid flow) is indicated by +++, less stronger by ++, just detectable by +, no observable by -. The MgO particle size ranges were obtained by wind sieving a milled sample of highly sintered "Degussa" magnesite.

The very fine power of the 0.05 - 0.1 micron fraction was a usual commercial product (" MgO levissimum", Messrs. Brocades, Amsterdam). The particle size in this case was measured by electron microscopic photographs.

TABLE I
DEFORMATION OF LiNaCO_3 - MgO PELLETS UNDER OWN WEIGHT
AFTER 24 HOURS OF HEATING AT 700°C . AND SUBSEQUENT
24 HOURS OF HEATING AT 850°C .
PELLET SIZES: 1.3 cm dia., 1.5 cm thickness

Particle size range MgO in microns	Weight % LiNaCO_3			
	20	30	40	50
0.05 - 0.1 (levissimum)	-	-	-	-
< 1 Degussa	-	-	-	+
1 - 3 "	-	-	-	+++
3 - 10 "	-	-	-	+++
10 - 25 "	-	-	+	+++
24 - 40 "	-	-	++	+++
30 - 100 "	-	-	+++	+++

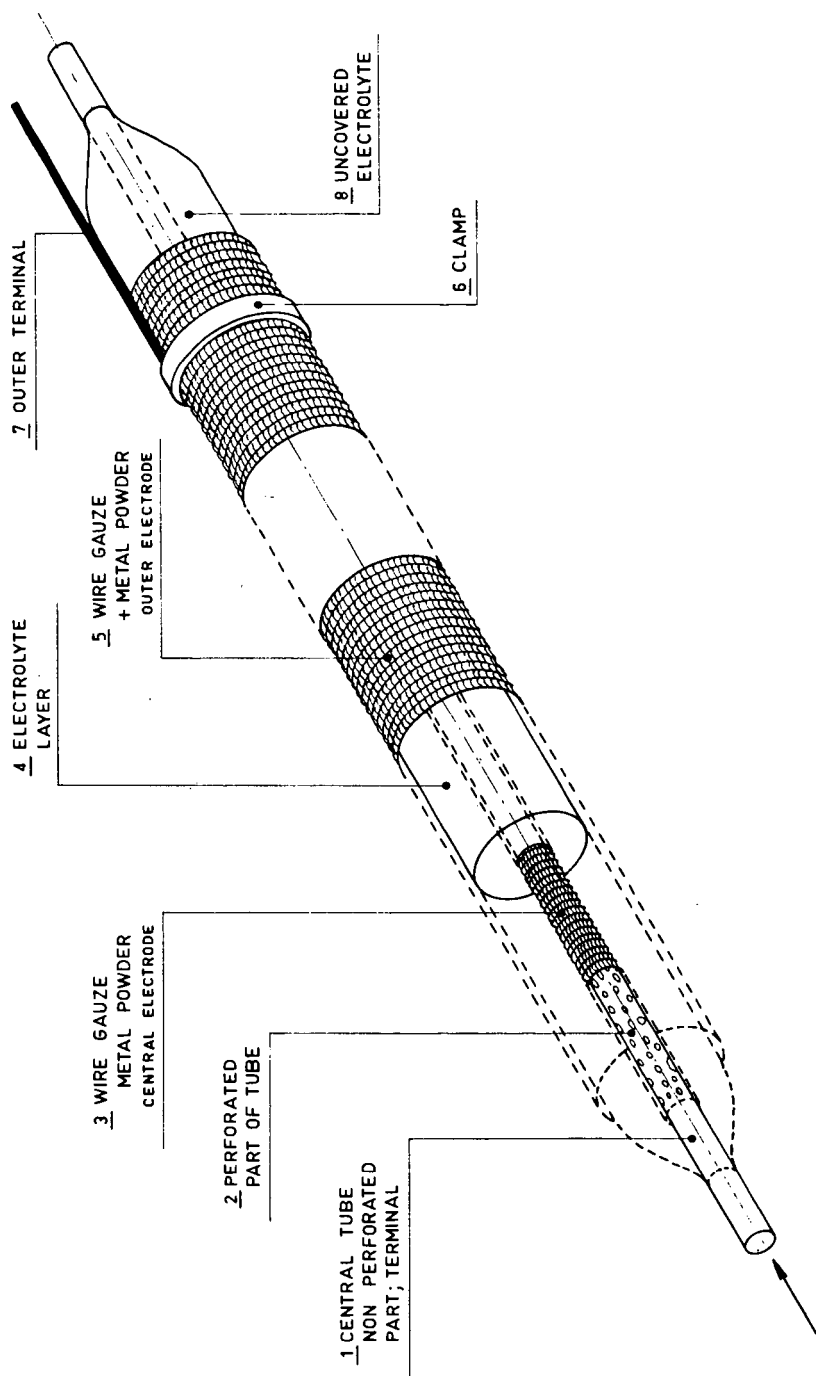


FIG. 3 EXAMPLE OF TUBE CELL CONSTRUCTION

The electrolyte paste is moulded around 2 and 3

Clearly, the finest powder is able to absorb the largest quantity of melt without plastic flow of the mixture. From the electrochemical standpoint, the use of fine powder is also favourable. First, the specific resistance of the mixtures with large melt contents will be low, and, second, the capillary forces retaining the melt inside the oxide matrix will be greatest in case the pores between the oxide particles are narrowest. The danger of electrode "drowning" thus becomes smaller in this case, and electrodes with correspondingly narrower pores might be used, yielding greater three phase zones.

So far, the "levissimum" powder has been used in further work. The great majority of the experiments was done with mixtures of this powder and carbonates in weight ratios ranging from 46/54 to 53/47.

By experiments of different kind, the following results and data were found.

1. LiNaCO_3 (m. p. 510°C .) may be substituted by lower melting combinations, such as equal parts of Li, Na and K carbonate (m. p. 390°C .), without observable change in mechanic deformability. Above the eutectic melting point, the substance is a stiff, white paste.

2. Cold-pressed and subsequently baked sheets of this paste are gas-tight at 700°C , under an excess gas pressure of 10 cm water column; layer thickness 0.2 cm, exposed area 1 cm^2 .

3. The specific conductivity of the paste is roughly 50%-70% of the pure liquid phase specific conductance (measured with 1000 c.p.s. alternating current). Fig. 1 shows a comparison of conductance vs. temperature curves of

- a. a pure carbonate melt,
- b. a 50 $\text{MgO}/50\text{ LiNaCO}_3$ paste, and
- c. a ceramic MgO frame impregnated with carbonate melt.

Although the absolute accuracy is probably not better than 20%, the superiority of the paste electrolyte is obvious.

4. The paste can be moulded into any shape. Different techniques can be applied. They include simple "hand"-moulding the hot substance by means of cooled metallic stamps or rolls (to which the paste does not stick), cold hydraulic pressing and subsequent baking, hot-pressing in chemically resistant moulds under relatively small pressures ($5\text{--}15\text{ kg/cm}^2$) and flame-spraying upon porous metallic layers such as wire gauzes impregnated with metal powders, perforated sheets and tubes and other electrode structures.

5. The internal porosity of the moulded substances in the cold state is small. It depends on the technique used. Representative figures are:

- Hand-moulding: 8%
- Cold-pressing* + baking: 14%
- Hot-pressing: 3%
- Flame-spraying: 8%.

*Hydraulically pressed at 1250 kg/cm^2 .

6. No high-purity MgO is needed if proper precautions are taken during the preparation stages. The latter comprises:

- a. mixing the components;
- b. heating the mixture at $600^\circ\text{--}700^\circ\text{C}$. as a first homogenizing step;
- c. grinding the loosely sintered product;
- d. a second heating, preferably in a CO_2 atmosphere, over a sufficiently long period as to allow completion of all chemical reactions of the fused carbonates with any impurity still present (CO_2 evolution must have stopped);
- e. when needed, a second grinding step of the now much denser product.

At stage e. and from thereon, take up of fresh impurities should be avoided.

7. The plastic flow under own weight of larger sized bodies is surprisingly small. A hot-pressed block of $5 \times 5 \times 14\text{ cm}$, weighing about 0.9 kg, was placed vertically upon a stainless steel support and heated in air at 700°C . during a 39 days' period (eutectic m. p. of the carbonates 390°C .). After this period, the length decrease was 0.1 cm or 0.7%. The weight decrease was 6.7 g or 0.75% (the steel support showing some chemical attack). The other dimensions of the block were found to be unchanged.

These results demonstrate the fairly favourable prospects for practical application of the paste electrolyte in high-temperature cells.

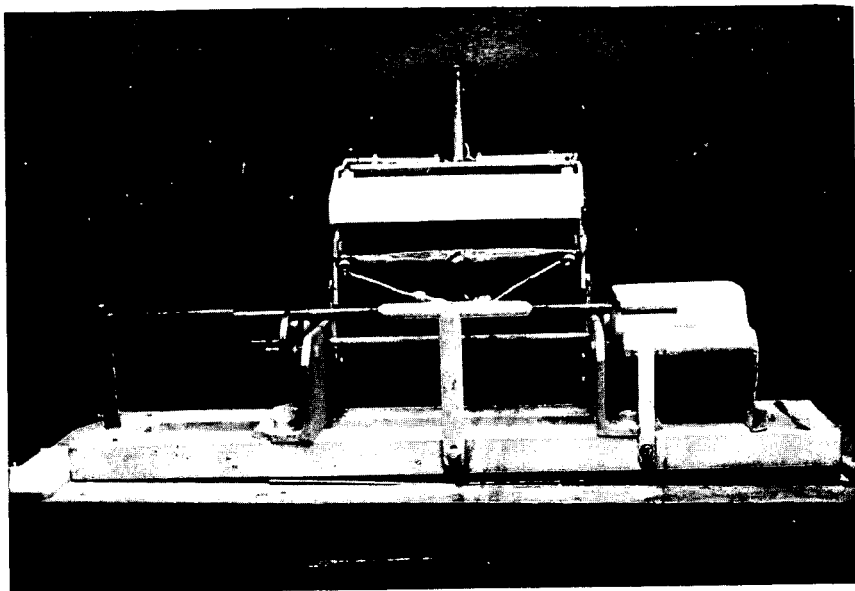


Fig.4 Installation for hot moulding of tube cell electrolytes.
Heating elements and surface nivellation roll
mounted in hinging support.

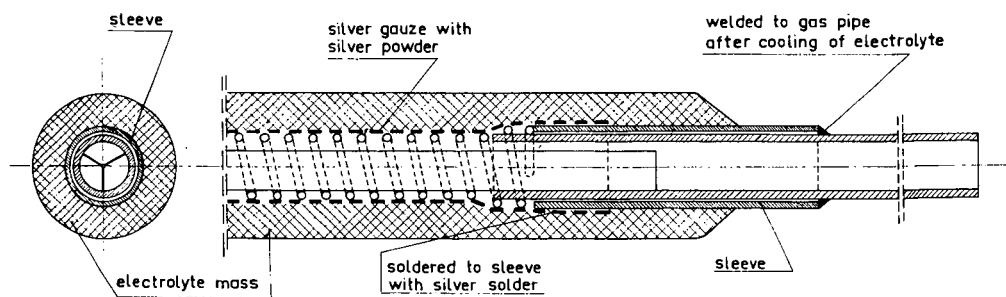


Fig.5 Modified tube cell construction, allowing free
contraction of the electrolyte upon cooling

III. SURVEY ON RESULTS WITH COMPLETE CELLS

A. Constructions

The "flexibility" of the paste electrolyte allows the construction of cells in various shapes. Whereas in the usual solid matrix arrangements an electrolyte disk is enclosed between gas spaces, (11) a reversal of this principle can be realized with relative ease, for instance when blocks can be manufactured in which canals are drilled out. The general concept of such a "canal cell" is shown in Fig. 2. It has been proposed already by Baur et al. (9) The advantage of the model is that no gasket materials (other than the paste itself) are needed. (To our knowledge, carbonate-resistant non-metallic gaskets are not known.) Of course, modified versions are thinkable, such as, for instance, mutually perpendicularly crossing air and fuel gas canals or a parallel arrangement of narrow rectangular cavities. In the latter case the model approaches a stack of disk cells in electric parallel connection.

Another model conceivable is the "tube cell", as shown in Fig. 3. In this case, the electrolyte is moulded around a central porous electrode and covered in turn by an outer electrode. Several of these cells may be placed in one single fuel gas (air) space, while air (fuel gas) is fed into the central electrodes. Again, no gasket materials in contact with the electrolyte are needed.

So far the majority of the experiments have been taken with single tube cells. No special attention has been directed towards the preparation of highly active electrode materials, the factor cell stability being considered as more important than the factor output in this stage of the research. Silver powder, embedded between the meshes of silver gauze, was used as air electrode in all experiments (based upon its excellent performance found in earlier research). Iron and nickel powders (or mixtures), obtained by reduction of the corresponding oxides, were used as fuel gas electrodes. No high-purity metals have been applied. In great lines, preparation and procedures with regard to the electrodes were similar to those described earlier.*

The tube cell construction is evident from Fig. 3. Moulding of the electrolyte paste around the central core (perforated tube + wire gauze with impregnated metal powder) can be performed in different ways. Simple hand-moulding by a procedure not unlike that of a glass-blower, namely alternate heating, addition of fresh material and surface nivellation with a cold metal sheet, was found quite effective in the hands of a skilled technician.** Flame-spraying the electrolyte powder directly onto the automatically rotating core, with surface nivellation by means of a cold aluminum roll, is a second possibility. It was found, however, that inhomogeneities were caused by the wind sieving action of the flame upon the powder constituents.

At present the electrolyte powder is sprinkled directly from a container onto the rotating core, which is heated by radiating elements. Surface nivellation again takes place on a cooled, freely rotatable aluminum roll. The present apparatus is pictured in Fig. 4. Some other methods, requiring less skill, are under study.

The only critical stage in the process is cooling the electrolyte body to ambient temperature. Because of the relatively larger thermal contraction of the electrolyte with respect to the perforated central tube of Fig. 3, the former is liable to occasional cracking.

A satisfactory solution to this problem is the spiral and sleeve construction shown in Fig. 5. The spiral is (slidingly) wound around the y-shaped support and connected to the sleeves. It carries the wire gauze - metal powder. The inlet tube fits rigidly around the y-support, but moves freely inside the sleeve. Free contraction of the cooling electrolyte is now possible by the flexibility in the length direction. In the cold state the sleeve is welded to the inlet.

The outer electrode may be constructed by wrapping a wire gauze "ribbon" in spiral turns around the electrolyte. Adjacent turns are spot-welded and the (slightly wetted) metal powder is pressed between the meshes afterwards.

For experiments the cell is enclosed in a long quartz tube, forming the outer gas space. The greater part is heated in a furnace, while the cold extremities are closed by rubber stoppers, allowing the gas-tight passage of the central pipe ends and other necessary objects (thermocouple, outer terminal, etc.). All experiments were carried out at atmospheric pressure.

*Compare, e.g., Ref. 1, p. 254, or Ref. 3, p. 83.

**The aid of Mr. J. Roele, technician of the Laboratory for Electrochemistry of the University of Amsterdam is greatly appreciated by the authors.

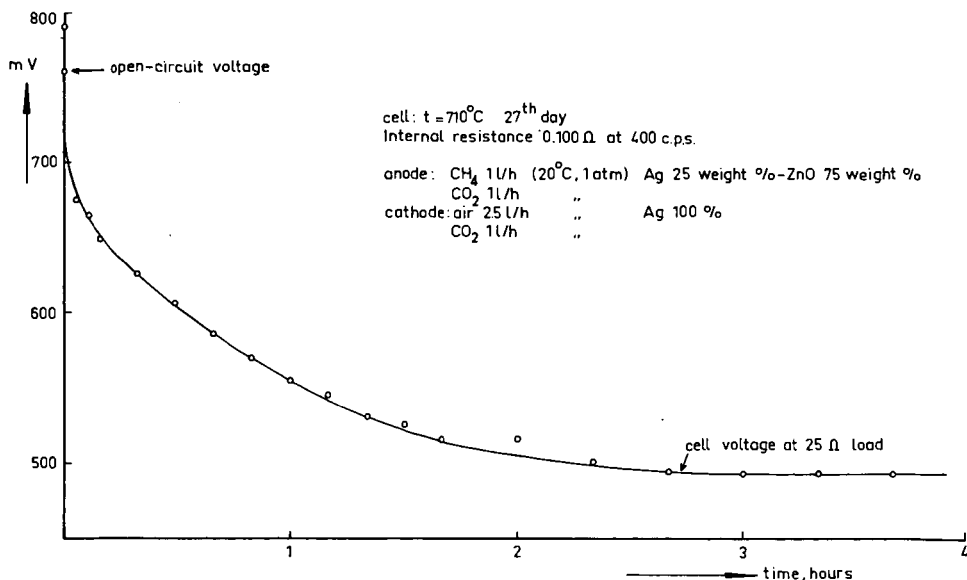


Fig. 6 . Slowness of the d.c. polarization processes

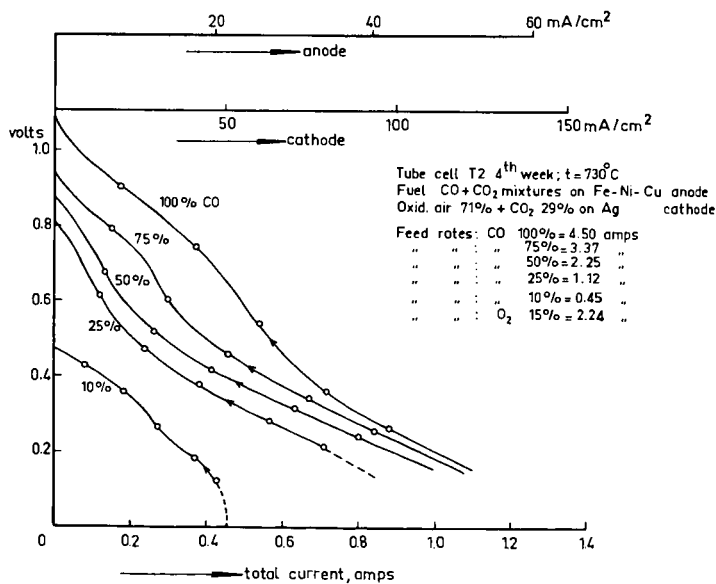


Fig. 7

Results with $\text{CO}-\text{CO}_2$ mixtures at 730°C
 In the 10% mixture, complete conversion is
 reached in one pass.

B. Experiments with Leak-Tight Cells

It was soon observed that the leak-tightness of these cells was considerably better than that of the formerly used ceramic disk cells. In some cases no leaks could be detected at all, even after two months of operation. (In fact, the maintenance of gas-tightness of the outer space was sometimes found to be more difficult than that of the paste.) Therefore, experiments could be undertaken which it was senseless to do with leaking cells.

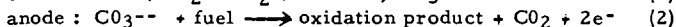
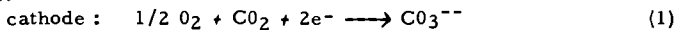
1. Fuel gases (CO , CH_3OH , H_2) could be "locked up" in the anode room at constant pressure and stationary temperature,* by means of a soap bubble membrane present in a calibrated tube connected to the gas outlet. It was found that in short duration tests the fuel gas volume increased at a rate directly proportional to the current drawn (within a few percents). There was a similar decrease in the cathode space, too, air + CO_2 being the oxidant. On open circuit, there was no volume changes. The rate of change was found to correspond with the theoretical figures in the case of air + CO_2 and CO + CO_2 . With hydrogen and methanol vapour the practical figures were smaller than those calculated, but this effect is probably due to condensation of H_2O in the cold ends of the cell. Obviously Faraday's law is obeyed.

2. In similar experiments of longer duration (approximately one hour) it could be shown that the discharge capacity of an iron-nickel-copper powder anode was definitely larger than the charge stored in the locked-up quantity of gaseous fuel. First, a continuous stream of gas was passed over the anode. Then this supply was stopped and current drawn (at constant load) from the cell till a low cut-off voltage (0.2 volt) was reached. The voltage vs. time curves were recorded. They did not show any pronounced breaks, pointing to changes in the anodic reactions during discharge. The quantity of gaseous fuel could be calculated from the volume and the temperature distribution in the anode space (1 equivalent gas = 1 Faraday = 26.8 Ah). Some typical data found are:

- a. CH_3OH 10 vol. % + CO_2 90 vol. % at 550°C .
(1 mole CH_3OH = 6 Faradays);
charge withdrawn from cell: 0.275 Ah;
charge in gaseous fuel 0.01 Ah; ratio: 27.5:1.
- b. CH_4 50 vol. % + CO_2 50 vol. % at 730°C .
(1 mole CH_4 = 8 Faradays);
charge withdrawn from cell: 0.57 Ah;
charge in gaseous fuel 0.45 Ah; ratio 1.26:1.

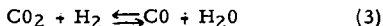
It is clear that either a chemisorbed phase is present, or that the metal powder is gradually oxidized. In the methanol case chemisorption of hydrogen is highly probable, whereas in the CH_4 case probably much less hydrogen is adsorbed. The significance of these experiments is that they prove that the "foregoing history" of electrodes may have a great influence upon their performance in later experiments, unless care is taken that really steady states are observed. Polarization curves measured under non-steady conditions are meaningless as a measure of cell performance. In some cases several hours are required before such a state is reached, as Fig. 6 may show.

3. In a steady state experiment CO_2 transport through the electrolyte was studied. The now commonly accepted overall electrode reactions for a carbonate electrolyte are:



These reactions were verified in a gas-tight cell with slightly wet H_2 as fuel and air + CO_2 as oxidants. The anodic products were led through CaCl_2 and soda lime tubes during one hour. The results are given in Table 2.

Since the water gas shift reaction:



will have practically no influence upon the composition of the anodic outlet (in the colder parts of the cell being in favour of $\text{CO}_2 + \text{H}_2$), the more than 90% "yields" of CO_2 and H_2O can be seen as a direct proof of reactions (1) and (2). To our knowledge such a proof has not been given earlier.

4. In earlier work** it was found that the open circuit voltage of cells operating on CO + CO_2 mixtures was very sensitive to oxygen leakage from the cathode. Thermodynamically calculated values are never reached in that case. Table 3 shows that very

*Temperature gradients could not be avoided. Before the experiments the gas spaces were flushed with similar gas mixtures.

**Compare Ref. 3, p. 90.

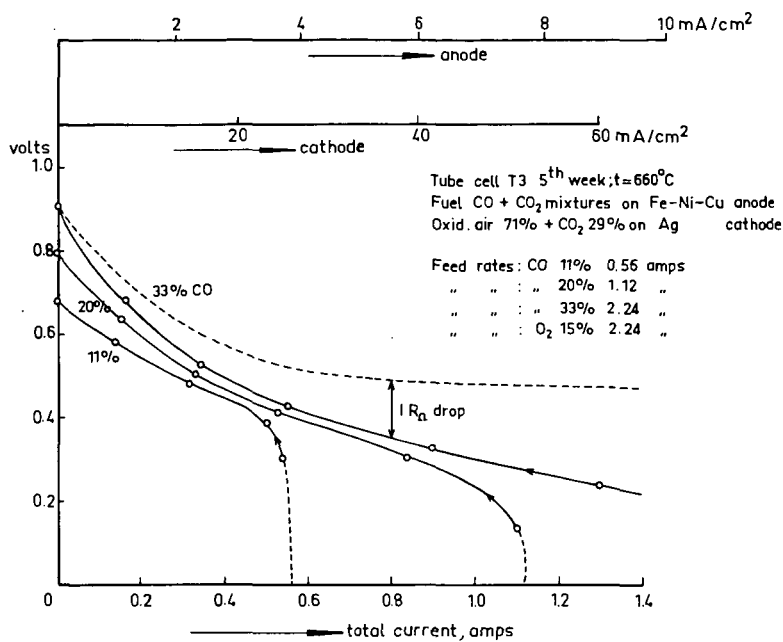


Fig. 8

$\text{CO} + \text{CO}_2$ mixtures at 660°C
 In the 11% and 20% mixtures,
 complete conversion is reached.
 Effect of ohmic drop shown in upper curve.

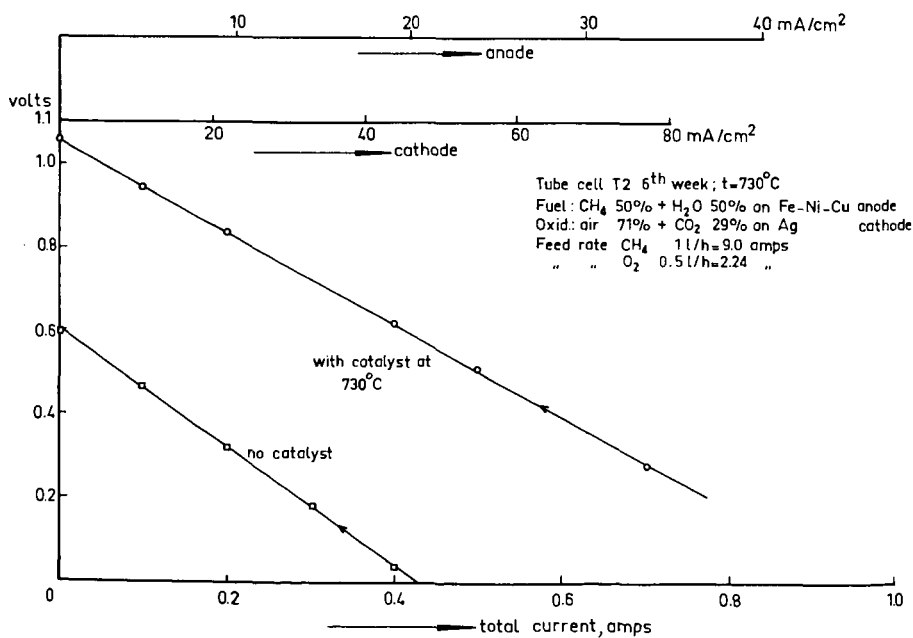


Fig. 9

Influence of nickel catalyst
 upon CH_4 -steam equilibrium
 and resulting cell performance.

good agreement is found in absence of leakage. Before the o. c. v. measurement the cell was discharged for some time.

TABLE 2
STEADY STATE CO₂ TRANSFER THROUGH A CARBONATE ELECTROLYTE AT 600°C.

Cell current at constant voltage : 0.332 A = 12.36 milli equivalents/hour			
Anode	H ₂ feed rate : 70.3 meq/h	anodic H ₂ O collected	: 12.90 meq/h
	H ₂ O " " : 1.60 "	" H ₂ O in feed	: <u>1.60</u> "
Cathode	O ₂ " " : 83.2 "	" H ₂ O by discharge	: 11.30 meq/h = 92% "yield"
	CO ₂ " " : 83.2 "	" CO ₂ collected	: 11.90 meq/h = 96% "yield"
H ₂ galvanically converted for 18%; O ₂ for 15%.			

TABLE 3
THEORETICAL AND PRACTICAL CELL OPEN CIRCUIT VOLTAGES ON CO + CO₂ MIXTURES AT 710°C.

CATHODIC GAS : air: 71.4 vol.% (O₂: 15.0 vol.%) CO₂: 28.6 vol.%

$$\text{NERNST EQUATION : } E_{\text{th.}} = E_o + \frac{RT}{2F} \ln \left[p^{\frac{1}{2}}(O_2)_c p(CO_2)_c p(CO)_a / p^2(CO_2)_a \right];$$

$$E_o (710^\circ\text{C}) = 1.020 \text{ V}$$

ANODE : Ag + ZnO; CATHODE : Ag

Volume % CO (CO ₂ = balance)	E calc.d. mV	E obs. mV	day of experiment
50	932	932	19th
25	885	881	9th
10	837	820	20th

C. Performance Data

Some steady state, total polarization curves (characteristics) are given in Figs. 7-10. The feed rates of fuel and oxygen (air used as oxidant) are expressed in amperes, for convenient comparison with the current drawn from the cell. The comparison with the current drawn from the cell. The compositions of the gas feeds are in volume percents; the feed rate of air - CO₂ was held constant (O₂ to CO₂ ratio 1:2). The inner electrodes were used as cathodes. Figs. 7 and 8 show results with CO - CO₂ mixtures in two cells of different anode geometry but with similar electrodes. It was found that this "similarity" of anodes usually gave far from identical results, in connection with the still primitive ways of contacting the powder metals with the outer electrolyte surfaces and the ill defined character of the metal particles. From the figures it can be seen that:

1. Anodic current densities are widely different, while cathodic ones are of the same order of magnitude.
2. At CO contents less than 20% the galvanic combustion can be virtually completed in one pass (at low c. d. in Fig. 8, but at >20 mA/cm² in Fig. 7). Obviously,

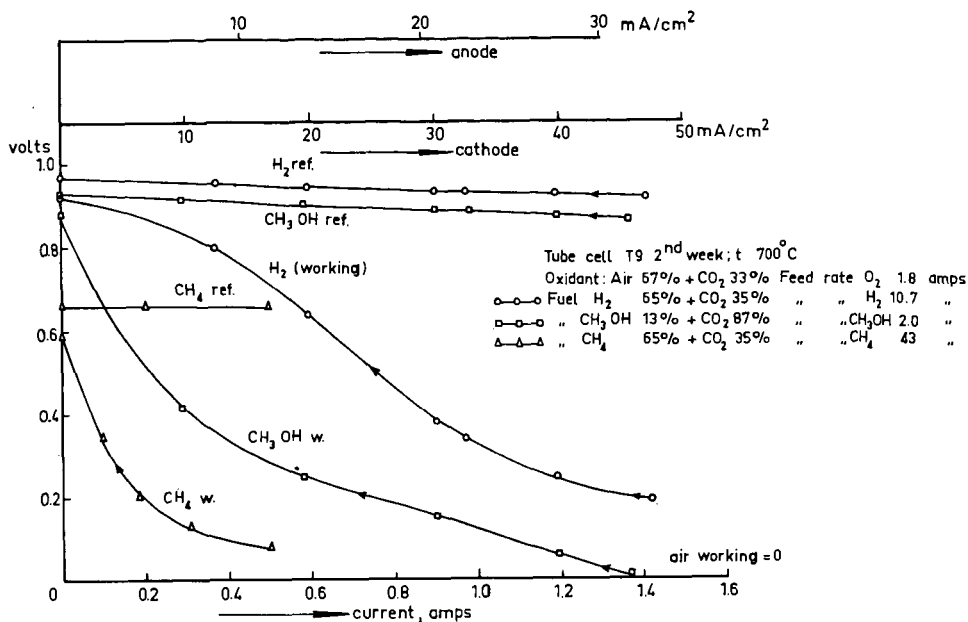


Fig. 10

Characteristics and electrode polarization on different fuels. Anode: "flaked nickel" cathode: silver. The cathode does not polarize at 4% final O₂ content.

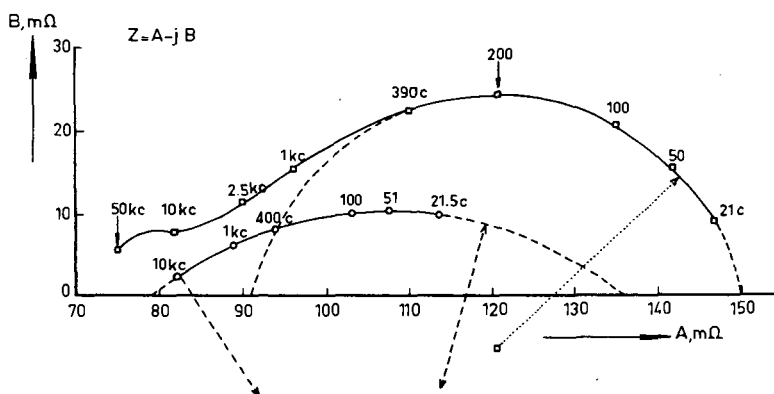


Fig. 11

Real vs. imaginary (Argand) diagrams of cell impedance $Z=A-jB$
 — Commercial dry cell at 20°C
 — Fuel cell at 700°C, on petroleum ether-CO₂ mixture. (no d.c. polarization)

the polarization caused by gaseous diffusion is extremely small, otherwise the observed limiting currents would have been smaller than those prescribed by the feed rate.

3. In the case of Fig. 7 there has been some leakage, which is evident from the fact that the open circuit voltages on low CO contents are definitely too low.

4. Polarization (to be ascribed to the anodes) is obvious, since the slopes of the curves correspond with effective resistances of 0.20 - 0.75 ohm, while the a. c. resistances at 1000 c. p. s. were less than 0.20 ohm (compare "ohmic drop" at the upper curve of Fig. 8). Fig. 9 shows results with a 50 - 50 vol. % CH₄-steam mixture, fed directly into the cell (lower characteristic) and passed first over a nickel-on-magnesite "reforming catalyst" at 730°C., respectively. Since the conversion percentage of the fuel remains below 10% at the maximal current (0.7 amp), most probably only hydrogen and CO have been galvanically oxidized in the catalyst experiment. Although the improvement is striking, it should be stressed that in practical batteries the necessary heat for the CH₄ conversion must be supplied by the battery itself, and not by external heat sources as in usual laboratory experiments.

(With higher hydrocarbons complete misinterpretation of characteristics may be caused by neglect of feed rate data, as is obviously the case in a fairly recent Russian publication. (12) The high temperature of the cell furnace will cause appreciable thermal dissociation into hydrogen and unsaturated compounds. From propane, for instance, 45 vol. % of H₂ can be formed at 700°C., which means that for a 1 amp current a feed rate as small as 0.55 l/h (20°C., 1 atm) is needed to run the cell on hydrogen only. For complete combustion only 45 ml/h of propane would be required.)

Fig. 10 pictures results obtained with a cell in which the anode was divided into two halves, about equal in area. One part served as reference electrode. The metal powder used in this case was "flaked nickel"*, particle size < 44 microns. The cathode (central electrode) was, as usual, silver powder. In the figure the potential of the cathode is taken as zero. Since the outer (anodic) space showed some leakage (not through the electrolyte), fuel supply rates had to be taken larger than usual. Clearly, only the anode is responsible for the polarization observed in all the presented figures. At a cell current of 1.4 amp (47 mA/cm² cathodic) the O₂ from the feed is converted for 78% and the final oxygen content is 4 vol. % without any significant polarization. The very poor performance of CH₄ (without extra catalysts) is obvious.

D. Canal Cells

A restricted number of experiments was made with this type. The cell performance depends greatly upon the quality of the electrolyte blocks and the proper insertion of canals and electrodes. Pore- and crack-free blocks are still difficult to prepare, though hot-pressing techniques have been used with some success. Blocks of 5 x 5 x 15 cm could be formed under 16 kg/cm², with a volume porosity of 2.5% - 5% in the cold state.

Contamination pick-up after the second preheating stage of the electrolyte material (cf. Sect. I) must be avoided, otherwise CO₂ bubbles are formed upon heating in the pressing mould. The cooling stage, especially the solidification temperature range, is quite critical with regard to crack formation. Canals can be drilled by cold tooling, but this procedure is unattractive in connection with the great hardness of the cold substance. Their formation in the hot state is under study. Cold, thin-walled metal tubes can be used to "cut out" canals in the hot substance if they are quickly inserted and withdrawn again. The insertion of electrodes in the canals also needs further study.

Experiments at 700°C., with a few, yet primitive models, in which some of the seven canals served as reference anodes and cathodes have learned that:

1. Polarization, apart from "ohmic drop", is completely due to the nickel powder (H₂) anodes used so far. Ohmic drops in the electrolyte are small: less than 80 mV at 50 mA/cm².

2. The silver powder (air + CO₂) cathodes remain unpolarized up to the point where the O₂ turnover is virtually in balance with the feed rate; that means, where the O₂ depletion is complete (verified at 50 to 100 mA/cm²). These facts are in full accordance with the tube cell results of Fig. 10.

3. The establishment of good electric contact between anode and electrolyte is of major importance for the power output. In this respect the cathodic contact seems to have less influence in the present apparent current density range (at least within certain limits).

*Manufactured by "Larsen Industries, Inc.", Murray, Utah, U. S. A.
(at presnet: United Techn. Industries).

4. The use of powder metal anodes with micropores (say <0.2 micron) leads to occasional flooding.

5. The shape of electrolyte blocks, used in two week experiments, remains unchanged.

E. Conclusions and Further Outlooks

It can be concluded that the use of paste electrolytes yields a significant improvement in the construction of permanently gas-tight cells. The consistency of the paste is such that the mechanical strength of the construction need not be borne by the electrodes only, as in liquid electrolyte cells. When the substance is crack-free in the initial (cold) state, it remains so during operation for at least 2-1/2 months, this period being the longest so far, during which single cells were tested. Chemical analyses of tube cell electrolytes, held in vertical position during two months, have revealed that no significant separation occurs of MgO and carbonates. (Differences in MgO content of 0.5% were observed between upper, middle and lower sections of a 20 cm tube.)

The silver powder cathodes of usually less than 0.1 mm thickness are almost ideal air electrodes, both in electric performance and long-run behaviour. The nature of this phenomenon is not yet understood completely.

Clearly, the fuel gas electrodes are the bottlenecks in further developments, although a perfectioning of electrolyte moulding techniques is also an important technological problem.

The study of anodic reaction mechanisms was taken up when sufficiently stable cells could be produced. A start has been made with a.c. measurements of electrode impedances as a function of frequency, in the range 20 c to 50 kc, by means of a modified Kelvin bridge technique. (This method enables an accurate determination of the very small impedances involved; magnitude less than 0.10 ohm.) A strong dependence upon frequency, gas composition and d.c. polarization was found in many cases. The interpretation of the results, which may proceed along general lines given by Euler and Dehmelt, (13) Euler (14) and Vetter (15), is fairly involved because of the ill defined state of the porous structures used so far. There is evidence of a slow (non-gaseous) diffusion process, probably coupled with a heterogeneous chemical reaction as being rate determining.

An example is given in Fig. 11, where the real components A of the cell impedance $A-jB$ is plotted against the imaginary B , with the frequency as parameter (Nyquist or Argand diagram). For comparison similar results are given, obtained with a commercial dry cell. In both cases there is evidence of a circular plot, which in the case of the dry cell can be largely explained by the parallel combination of a constant double layer capacity and a constant resistance associated with a slow electrochemical exchange reaction at the zinc electrode, (13) In the fuel cell case (the center of the circle being situated much lower) the equivalent circuit seems to be composed of a "Warburg impedance" (which is caused by diffusion) in parallel with a constant resistance, presumably also related to exchange processes. It should be said, however, that plots of various course have been found with different cells, even when the anodes were "similar".

Therefore, another approach has been made recently, in which the behaviour of better defined anode materials will be studied.

The impedance behaviour of the present silver cathodes escapes detection with the bridge; presumably the reactions are too fast to be followed in the mentioned frequency range.

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